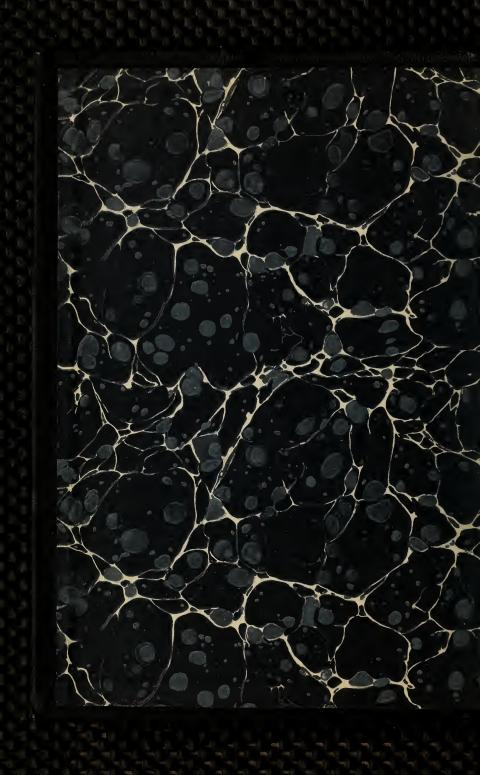
NIST

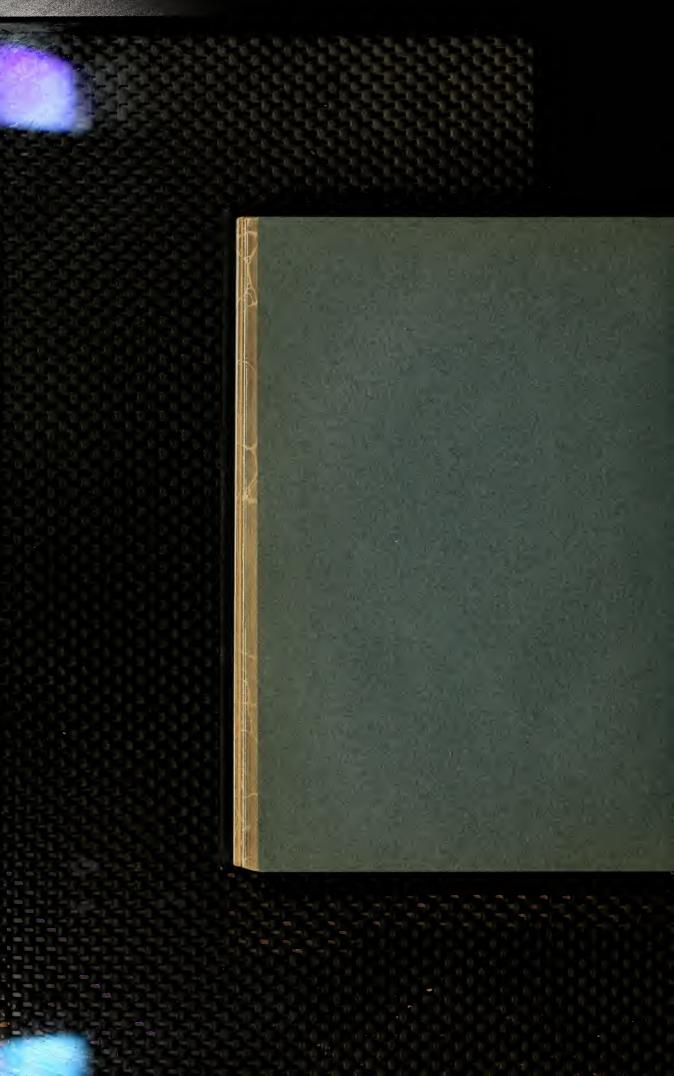
A11102 163058

NATL INST OF STANDARDS & TECH R.I.C.

A11102163058

Technologic papers of the Bureau of Sta
11.U4 v51-57-1915 C.1 N85-PUB-C 1910





DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 53

AN INVESTIGATION OF FUSIBLE TIN BOILER PLUGS

BY

GEORGE K. BURGESS, Physicist and PAUL D. MERICA, Assistant Physicist

Ruranu of Standards

Bureau of Standards

ISSUED OCTOBER 15, 1915



WASHINGTON GOVERNMENT PRINTING OFFICE 1915

TECHNOLOGIC PAPERS
t. The Effect of Preliminary Heat Treatment upon the Drying of Clays
2. The Strength of Reinforced-Concrete Beams—Results of Tests of 333 Beams (first series) (200 pp.)
3. Tests of the Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, Together with Tests of Damp-Proofing and Water-
Proofing Compounds and Materials (127 pp.)
Mineral Lubricating Oils (14 pp.)
Cement Mortar and Concrete (25 pp.)
Steels (6 pp.)
A. V. Bleininger and G. H. Brown 8. A Rapid Method for the Determination of Variadium in Steels, Ores, etc.,
Based on Its Quantitative Inclusion by the Phosphomolybdate Precipitate (20 pp.)
o. Density and Thermal Expansion of Linseed Oil and Turpentine (27 pp.).
H. W. Bearce 10. Melting Points of Fire Bricks (17 pp.)
Ralph P. Devries 12. Action of the Salts in Alkali Water and Sea Water on Cements (157 pp.)
P. H. Bates, A. J. Phillips, and R. J. Wig 13. The Evaporation Test for Mineral Lubricating and Transformer Oils (13 pp.) C. E. Waters
14. Legal Specifications for Illuminating Gas (31 pp.). E. B. Rosa and R. S. McBride 15. Surface Insulation of Pipes as a Means of Preventing Electrolysis (44 pp.)
Burton McCollum and O. S. Peters 16. Manufacture of Lime 130 pp.)
G. H. Brown and G. A. Murray 18. Electrolysis in Concrete (137 pp.). E. B. Rosa, Burton McCollum, and O. S. Peters
19. Physical Testing of Cotton Yarns (31 pp.)
R. S. McBride and E. R. Weaver G. H. Brown and E. T. Montgomery
22. Effect of Overfiring upon the Structure of Clays (23 pp.)
24. Determination of Phosphorus in Steels Containing Vanadium (11 pp.)
25. Electrolytic Corrosion of Iron in Soils (69 pp.). Burton McCollum and K. H. Logan 26. Earth Resistance and Its Relation to Electrolysis of Underground Structures. Burton McCollum and K. H. Logan
(Continued on page 3 of cover)



Bureau of Standards Technologic Paper No. 53



Fig. 1.—Fusible tin boiler plug

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 53

AN INVESTIGATION OF FUSIBLE TIN BOILER PLUGS

BY

GEORGE K. BURGESS, Physicist
and
PAUL D. MERICA, Assistant Physicist
Bureau of Standards

ISSUED OCTOBER 15, 1915



WASHINGTON GOVERNMENT PRINTING OFFICE 1915 ADDITIONAL COPIES
OF THIS PUBLICATION MAY BE PROCURED FROM
THE SUPERINTENDENT OF DOCUMENTS
GOVERNMENT PRINTING OFFICE
WASHINGTON, D. C.
AT
20 CENTS PER COPY

AN INVESTIGATION OF FUSIBLE TIN BOILER PLUGS

By George K. Burgess and Paul D. Merica

CONTENTS

		Page
I.	Introduction	3
	Specifications for fusible tin boiler plugs	4
II.	Examination and investigation of plugs	5
	Design and construction	6
	2. Types of deterioration	7
	3. Purity of tin and relation to deterioration	10
	4. Theory of "network" type of oxidation	15
	5. Testing of theory by service tests at Bureau	10
III.	Testing of the purity of tin	22
	Conclusions.	25
	r. Summary	27
	Appendixes	28
	Appendix r.—Analyses of pig tin by Cowan	28
	Appendix 2.—Existing specifications for fusible tin boiler plugs	30
	Appendix 3.—Specifications of Steamboat-Inspection Service in force	Ŭ
	July, 1914	34
	3 37-7-1	37

I. INTRODUCTION

The fusible boiler plug in its usual form consists of a brass or bronze casing with external pipe thread, filled from end to end with a fusible metal or metal composition, which has a melting point around 200° C (390° F); two such plugs are shown in Fig. 1. These are fitted at various places into the boiler, either in the flues, tubes, or combustion chamber, in such a position, however, that they are about 1 inch or more above the dangerous low-water level, with one end on the fire and one end on the water side. As long as the water level in the boiler is above these plugs the temperature of the latter remains below the melting point of the filling (at 150 pounds boiler pressure the temperature is about 180° C or 357° F), but if the water falls much below the level of the plug, opportunity is given for a local overheating in the

vicinity of the plug. The filling of the plug then melts and is blown out.

The fusible plug seems to be an old English invention and to have been in use for many years. It has, in fact, been required to be installed in all steam vessels of the American merchant marine since 1852, and is now required in all boilers except pipe, flash, or coil boilers on vessels subject to inspection by the Steamboat Inspection Service, Department of Commerce. This inspection includes approximately 11 850 boilers requiring installation of boiler plugs.

Fusible plugs are also used elsewhere than in boilers of the American merchant marine. They are used in many but not all factory and locomotive boilers in this country and abroad, but

are not generally used in marine boilers abroad.

They are also not used in the United States naval service, the practice there not favoring the installation of safety devices of any sort, fusible plugs or otherwise, as it is considered that there presence fosters negligence. This opinion—at least in so far as it concerns boiler plugs—appears to be shared also by many railroad authorities.

1. SPECIFICATIONS FOR FUSIBLE TIN BOILER PLUGS

Four typical sets of specifications for fusible tin boiler plugs are given in Appendixes 2 and 3. In Appendix 2 are given the existing specifications of the Steamboat Inspection Service, of the Interstate Commerce Commission, and the recommended specifications of the American Society of Mechanical Engineers. In Appendix 3 are given the specifications of the Steamboat-Inspection Service in force in July, 1914, at the time the present investigation was begun.

Tin seems to be the metal used at present almost exclusively as the fusible constituent of such plugs, and is required by the above specifications. It would seem to be in this respect a desirable metal, having a low melting point, being only slightly corrodible and easily obtained pure. Its desirability in this respect is nevertheless to some extent called in question by the results of the investigational survey of fusible tin boiler plugs, which was

made at this Bureau, from June, 1914, to March, 1915. These specifications will be referred to again briefly in Section II, and also in Section IV after describing the experiments at this Bureau.

II. EXAMINATION AND INVESTIGATION OF PLUGS

On May 11, 1914, a boiler of the steamship *Jefferson* exploded, causing the loss of life of several persons. Investigation showed this explosion to have been due to low water and consequent overheating of the boiler plates. This should have been indicated by the melting of the filling of the Banka tin plug in that region, which plug, however, was found to be unmelted and apparently or at least superficially sound.

At the suggestion of the Secretary of Commerce, this plug was sent to this Bureau for determination of its cause of failure. It was sawed open longitudinally and was found to contain traces only of the original tin, embedded in a dirty, greenish-white matrix. A photograph of this central longitudinal section is shown in Fig. 2, in which the light regions represent the remaining tin. The matrix was found to be largely tin oxide, SnO₂, which upon test showed a melting point above 1600° C (about 2900° F). This oxide was distributed in such a form and quantity that it held the pressure of the boiler, and would not have melted until the bronze of the casing and even the steel of the boiler had melted. When reliance is placed upon such a plug to give warning of dangerous boiler conditions it is to be looked upon as an actual source of danger instead of safety.

The question arose then, To what is the presence of tin oxide to be ascribed; was it there originally; has it been formed by corrosion; and, if so, is the cause for its comparatively rare occurrence in such plugs to be sought wholly in the different operating conditions of the boilers, or is a fault in the method of manufacture of these plugs at least partially responsible? A search in the literature failed to reveal any reference to failures of fusible tin plugs of this sort, except vague statements that they were not entirely reliable, due to the formation of boiler scale on the inside and soot on the outside, and a statement that the filling was likely to change its melting point during service. No data could be found concerning the oxidation of tin at higher temperatures.

A request was then made to the Steamboat-Inspection Service that more plugs be sent to the Bureau for test, both new plugs and also those which had been removed by the inspectors, in order that by an inspection of these plugs information might be obtained bearing on the points raised above. In answer to the request 1050 plugs were received, of which about 100 had been in service varying from 4 to 12 months, and representing the products of 105 firms.

These plugs were first examined to ascertain whether their dimensions corresponded to the specifications of the Steamboat-Inspection Service. They were then sawed open axially through the center and the form and condition of the filling observed, particular attention being paid to the presence of oxide, scoriae, blowholes, and other faults originating either in the manufacture of the plugs or during their service.

1. DESIGN AND CONSTRUCTION

The specifications require certain minimum values of the diameter of the tin filling at both ends. In three plugs from three firms these dimensions were less by one sixty-fourth inch than the prescribed value.

The specifications in force at the time these plugs were manufactured called for a bore "tapering evenly from end to end of filling." (See Appendix 3.) Of 1033 plugs examined in this respect, 97 did not correspond to this specification. These were manufactured by 30 firms. Of these, 27 contained fillings having ribs projecting into the casing, 3 contained threaded fillings, and 22 contained fillings which were not tapered along their entire length. In four plugs from the same manufacturer the bore of the casing had not been machined after casting and the filling could be easily dislodged from the casing.

It may be noted here that the correct design of such a plug is of more importance than might be casually supposed. It is shown below that, owing to the difference in the coefficients of expansion of the casing and of the filling of such a plug and to the existence of an allotropic change in tin at about 160° C (320° F), there will be interplay between casing and filling unless

the design is such as to support the filling rigidly in the casing and unless the adhesion between the two is excellent.

A smooth bore "tapering evenly from end to end" is from this consideration not to be recommended, and, indeed, the Steamboat-Inspection Service has recently allowed a fine inside thread. It is hardly evident, however, why a thread should be allowed, and not other types of recess or projecting shoulder, to keep the tin filling rigidly in place.

The new plugs, about 950 in number, were all of sound appearance, and none showed the presence of oxide or scoriae in the tin filling. A number of the plugs contained minute blowholes, and about 10 of the 950 plugs showed blowholes of from $\frac{1}{16}$ inch in diameter. The inner surface of these blowholes was always clean and bright.

2. TYPES OF DETERIORATION

The condition of the tin in the plugs which had been in service varied greatly. A few of the fillings were piped or showed blowholes, the surfaces of which were clean and bright.

- 1. There were 22 plugs from 10 firms which showed sound fillings that had remained apparently absolutely unchanged after a service of 12 months in most cases.
- 2. In 47 plugs from 21 firms the filling had been partially melted away at the fire end, as shown in Figs. 3 and 4. The fillings were otherwise sound. In about 10 of these plugs a scale of oxide coating had been left on the inside of the casing bore as can be seen in Fig. 4. In the other cases the fire end of the casing bore was clean.
- 3. In 11 plugs from 6 firms (besides those of class 5 (a) below) the filling had expanded and protruded at the fire end (small end) or at both ends. This is shown in Figs. 5, 6, and 12. The fillings were sound except that in 9 cases a layer of oxide was to be found between the casing and filling, as is shown in Fig. 7. This layer is usually seen to start from the fire end. The oxidation at the edge of the filling was probably preceded by a loosening of the plug in its casing which allowed access of flue gases. This is discussed below.

- 4. Seven plugs were either corroded or pressed in at the water end, the appearance of one of which is shown in Fig. 8. Although the inside surfaces of the tin were sometimes corroded, it is probable that this peculiar form had been assumed under the pressure of the boiler while the tin was at a temperature at which it was semiplastic, i. e., between 195° and 230° C. In one case the tool marks could still be seen on the inside (water side) surface, which was sunk about 5 mm. at the center.
- 5. In 14 plugs, from 8 firms, nonmetallic inclosures or incrustations were found in the filling. Since this mass was found to be in most cases, where not otherwise noted, practically pure tin oxide, SnO2, contaminated at times with traces of ZnO and CuO, it will hereafter be referred to as it was under (2) and (3) as "oxide." This oxide occurred in several forms.
- (a) In 4 plugs from one firm the oxide was practically pure SnO₂ with traces of zinc and lead and no traces of sulphates, chlorides, or nitrates, and occurred in the form of a network, proceeding from the water end toward the fire end. This type is shown in Figs. 9, 10, 11, 12, and 13, which show successive stages of the progress of the oxidation. Of these Fig. 9 is of plug No. 56, Figs. 10 and 11 of plug No. 872, and Figs. 12 and 13 of plug No. 40. The original plug from a boiler of the steamship Jefferson shows a very much more advanced state of this type of oxidation. (See Fig. 2.)

It is obvious from the following considerations that this oxidation occurred in service and that the oxide was not poured in with the tin originally:

- The plug is always expanded outward at oxidized end.
 The oxidation always starts from the water end of plug and becomes less marked toward the fire end.
- (3) This oxide is immediately visible upon exposing a surface of the "tin," and a plug containing it in this form could not escape rejection when the plug ends were machine finished.
- (4) It has been attempted and not found possible to pour tin plugs in which oxide veins or granules of such coarse texture are visible. In such attempts to do this the tin was first badly oxidized and then poured at temperatures varying from about 300° to 500° C (600° to 900° F).

(b) In 10 plugs from 7 firms the fire end of the plug was filled for a third to one-half of the distance from the end with a solid adherent mass of what was in many cases impure oxide of tin with traces of sulphates, zinc, lead, and copper. The characteristic appearances of these plugs are shown in Figs. 14, 15, 16, 17, and 18.

6. Two plugs had the appearance shown in Fig. 19. These plugs had evidently been arrested by the inrush of "cold" water in the very act of blowing out while at a temperature in which they were semiplastic.

The classification here described is summarized in Table 1.

TABLE 1
Types of Deterioration

Condition of plug or type of deterioration	Plugs be- longing to category of column 1	Manufac- turers whose products belonged to class of column 1
1. Filling sound.	22	10
2. Filling sound, but partially melted away	47	21
3. Filling expanded	11	6
4. Filling corroded or pressed in at water end	7	3
5, a. Filling had undergone "network oxidation"	4	1
5, b. Filling partially gone and casing filled partly with nonmetallic matter,		
oxide of tin, plaster of Paris, etc	10	7
6. Fillings arrested in blowing out	2	2

It was evident that of the approximately 100 used plugs examined only 7 contained the incrustation or oxides in sufficient quantity and in a form which would have prevented the blowing out of the plug at the melting point of tin. These were plugs 40, shown in Figs. 12 and 13; 43, similar to 40; 9, shown in Fig 14; 27, shown in Fig. 16; 122, shown in Fig. 15; 1045, shown in Fig. 17; and 1047, similar to No. 1045.

In all of these cases the incrustation or the network of oxide would probably have held the boiler pressure even after the melting of the tin which still remained in the plug. These plugs were dangerous plugs.

3. PURITY OF TIN AND RELATION TO DETERIORATION

In order to relate, if possible, the types of failures just enumerated to the purity of the tin in the fillings, the melting point of a number of the used plugs as well as of the new ones was taken. It is well known that the presence of metallic impurities changes the melting point of a pure metal, and, indeed, the melting point may be used, as it was in this case, as a criterion of the purity of a metal. Impurities in small amounts, such as lead, zinc, bismuth, cadmium, and copper, lower the melting point of tin, whereas iron and antimony raise it. (See Bornemann, Die binären Metal legierungen, 1909–1912.)

As very little material was available from a plug, these determinations had to be made with small quantities; therefore several were made with a modified form of the micropyrometer, described in this Bureau's Scientific Papers Nos. 198 and 205, by Burgess and by Burgess and Waltenberg, respectively, in which method only a minute amount of material is required. As the optical pyrometer could not be used at this temperature, these determinations were made by calibration of platinum strip temperatures in terms of heating current. This was done for temperatures of 231°.9 C (melting point of tin), 271° C (bismuth), and 320°.9 C (cadmium). For each determination minute pieces of "Kahlbaum" tin (highest grade of purity) and of the tin for test were placed side by side on the platinum strip and observed by perpendicularly reflected light through a microscope.

The current through the platinum strip was gradually increased, and by noting the values of the current at which the pure and the test tin melted, respectively, the difference between their melting points could be computed from the calibration curve of platinum strip temperature and heating current. This method was satis factory only for small differences of temperature of one or two degrees and was in no case as accurate as the other determinations described below.

The majority of the thermal purity tests, however, were made as freezing point determinations by a direct cooling curve method

¹ Bulletin Bureau of Standards, 9, p. 475, 1913; and 10, p. 1, 1913.

requiring only 2 or 3 grams of the material. A small glass tube of about 6 mm diameter was fused shut at one end and 2 or 3 grams of the tin sample to be tested was inserted and melted at the bottom of the tube. A copper-constantan thermocouple. made of wires of 0.3 mm diameter inclosed in a much smaller. thin-walled glass tube, was then placed in the molten tin, and the larger tube with tin and thermocouple immersed in an oil bath, 15 cm deep, which was heated with a Bunsen flame. The ends of the couple were attached through ice-cold junctions to either a potentiometer or a milli-voltmeter of high resistance, 400 ohms. by which the emf of the thermocouple could be measured. The temperature of the bath was then allowed to fall, by removing the Bunsen flame, and readings of the emf were taken every 15 seconds on the potentiometer. The curves of time and emf so taken showed well-defined arrests in all cases except for those with a large percentage of impurity (for example, there was 8 per cent lead in one case) when the solidification took place over a wide temperature interval. The values obtained in taking one of the cooling curves of pure "Kahlbaum" tin are given below.

Freezing of Pure Tin

[Potentiometer (emf) readings taken every 15 seconds]

Millivolts	Differences	Millivolts	Differences	Millivolts	Differences
10.19	0.03	9.99	0.01	9.97	0.01
10.16	.04	9.98	.00	9,96	.03
10.12	.03	9.98	.00	9.93	.02
10.09	.04	9.98	.00	9.91	.02
10.05	.04	9,98	.00	9.89	.06
10.01	.02	9.98	.01	9,83	
ŀ]	l			

The "freezing" point of this sample was at the "arrest" at 9.98 millivolts. The thermocouple was calibrated under the same conditions at the steam point (about 100° C) and at the melting point of pure Kahlbaum tin taken at 231.9° C. The values on fairly pure tin could be repeated generally to within ±0.01 millivolt or within ±0.15° C, and in fact the arrests on successive cooling curves of Kahlbaum tin repeated more closely.

Chemical analyses were then made on some of the samples to check the results of the thermal data.

In Table 2 are given various characteristics of the fusible plugs examined, including time of service, freezing point, chemical analysis, and reference to photographs. The manufacturers are represented by letters in column 3.

TABLE 2 Characteristics of Fusible Plugs

	Months			Freezing	Che	mical anal	ysls b		
Plug	Plug	in service	Steamship	Manufac- turer	point of tin filling °C a	Zinc	Lead	Other metals	Photo- graph
1		USED PLUGS Class 1.—Plugs Apparently Sound After Service			Per cent	Per cent	Per cent		
80	12	Verne Swain	A	232. 2					
88	12	Sunshine	В	231.4					
89	12	do	В	228. 2	0.2	1.3			
109	12	Waterford	С	228. 6	.6	.5			
870	3	Panama	С	c 229	Trace	Trace	0		
871	4	Tug 20, N. Y. C	С	c 228.5	Trace	Trace	0		
873	4	do	С	c 229	Trace	Trace	Trace Cu		
1035		Seaboard	С	227.4	1.8	Trace			
1036		do	С	226.8	1.3	.1			
1037		do	С	226.8	.9	.2			
1039	4	West Farms	С	229. 8	.7	Trace			
1048		Tug S. Q. Brown	P	229.0	.3	.7			
1049		do	P	228.4	.3	1.2			
1050		do	P	228.3	.4	.8			
		the Filling was Partially Melted Out at the Fire End							
102				230. 2					
2	8	Andasti	D	230. 8					
3	6	Geo. B. Leonard	E	229. 8					
5	5	Sir T. Shaughnessy	F	230.3					
6	7	Jas. T. Martin	D	228. 4	.8	.1			
7	7	Joe D. Morrow	G	230.1					
10	8	Kniskle Bros	D	230.6					
19	12	Game Cock	H	229.4	.6	.4			

a Pure Kahlbaum tin, Banka tin, and Straits tin have a freezing point at 231.0° C.
b Blanks signify that no analysis was made for the metal or metals in that column. The group "Other metals' includes silver, mercury, copper, bismuth, autimony, arsenic, iron, aluminum, chromium, nickel, mangances, and magnesium.
c These determinations are accurate only within ±1.0°.

TABLE 2—Continued

	Months	Manufac-	Freezing	Che				
Plug	in		point of tin filling °C	Zinc	Lead	Other metals	Photo- graph	
		USED PLUGS—Contd						
		Class 2-Continued			Per cent	Per cent	Per cent	
20	5	F. B. Jones	H	228.6	-7	.2	rer cent	
23	12	Dallas City	H	229. 8				
50		Chesapeake	1	231. 4				
94	5	Columbia	J	230, 4				
99	12	Huron	K	230.4				Ø
1030	3	Jamestown	L	232.0				
1031	3	do	L	231. 9				
1032	3	do	D	230. 0				
1044	3	Alaskan	R	229. 6	.5	.7		
1046	3	do	R	230.0	.6	.8		
1010		Class 3		230.0				
81	12	Verne Swain	A	230. 1				
57	12	City of Atlanta	С	230.3				
69	12	Red Spot	M	231. 1				
71	12	Spottsville	M	231.9				
82	12	C. H. Organ	A	231.0				
68	12	S. P. Gillett	N	231. 9				
84	12	C. H. Organ	A	230. 3				Ü
83	12	đo	A	229.0				
85	12	đo	A	231.9				
48			0	230.3				
72	12	Commerce	P	228. 7	. 10	1,00		
		Class 4.—Plugs Corroded or Pressed in at Water End		22011				
19	12	Game Cock	H	229. 4	.6	.4		
20	5	F. B. Jones	н	228.6	.7	.2		
		Class 5.—Plugs Contain- ing Oxide						
		Subclass (a), Network oxide						
40	12	Gowanus	С	230	.5	Trace	0	{
43	12	do	С	225	3.5	0	0	Ì
56	12	City of Augusta	c	229. 9	.4			
							إناسيا	ſ
872	3	Tug 20, N. Y. C	С	225	4.2	0	0	1

TABLE 2-Continued

	Months		Manufac-	Freezing		mical anal	Divido	
Plug	in service	Steamship	turer	point of tin filling °C	Zinc	Lead	Other metals	Photo- graph .
		USED PLUGS-Contd						
		Class 5—Continued						
		Subclass (b), Containing solid "oxide" or other						
		nonmetallic inclusion			Per cent	Per cent	Per cent	
9	8	Kniskle Bros	D	230. 0				14
27	3	Shaver	H	228. 6	.8	.3	0	16
122	12	J. A. Carney	H	231. 9	0	0	0	15
1045	3	Alaskan	R	230. 2	•6	.2		17
1047	3	do	R	228. 0	1.0	.6		
20	5	F. B. Jones	H	228. 6	-7	.2		
59	12	Clevedon	P	224. 6		•••••		18
73 18	12	Bailey Gatzert	T	228. 2				
18	12	Bailey Gatzert	1	228.8				
		NEW PLUGS						
1034				230.8				
1038				228.3	.9	Trace		
1051				230. 2				
637				c 230				
529				230.6	0	Trace	Trace Cu	
505				c 231				
479				c 230				
476				c 229				
444				c 230				
427				c 231				
421				231	0	Trace	Trace Cu	
285 272				c 229 c 221	•••••			
272				¢ 221				
190				c 232				
185				229		8.3		22
178				¢ 230		0.3		26
145				c 229				
186				225		3.1		
187				228		1.9		
101				220		1.9		

A consideration of the above table shows the following facts:

⁽a) Banka tin, as required in the specifications above, was not and is not being used in the filling of a considerable number of the plugs. Analyses of four samples of Banka tin by W. A.

*Cowan 2 showed the tin content to be 99.93, 99.97, 99.96, and 99.96 per cent, respectively, by difference. (See Appendix 1.)

Of about 70 melting-point determinations made on used and new plugs only 11 gave values within 0°.5 C of the melting point of pure Kahlbaum, Banka, or Straits tin.

Of 35 plugs analyzed chemically only 6 fillings showed 0.20 per cent or less impurities, or, in other words, only 6 of 35 glug fillings examined chemically were composed of any variety of high-grade tin. (See paragraph below.)

(b) The principal impurities are lead and zinc. It may be noted that it is not possible that the zinc or lead, in amounts greater than the solubility of these metals, respectively, in tin at high temperatures (180° to 190° C), could have come from the bronze casing by diffusion in the solid state. By solubility is meant here the amounts of these metals which actually dissolve in the tin to form a homogeneous solid solution.

(c) The table shows that classes 1, 2, 3, and 5 (b) (p. 7) contain plugs having impure tin as well as those containing pure tin (i. e., of melting point of 231°.9). Impure tin is then *not always* a cause of oxidation or deterioration in these plugs.

(d) All of the four plugs, as well as the plug from the boiler of the steamship Jefferson mentioned on page 5, showing the network type of oxide, came from the same manufacturer, were used on four different vessels, had low melting points, and contained zinc.

4. THEORY OF "NETWORK" TYPE OF OXIDATION

An explanation of this type of failure may be found in the effect of the zinc upon the process of oxidation of the zinc-tin alloy and a consideration of the constitution of the Sn–Zn alloys will throw some light upon this peculiar phenomenon.

The equilibrium diagram, according to Guertler, is shown in Fig. 20, from which it can be seen that the solubility of zinc in tin is very small in the solid state, less probably than 0.2 per cent.

² Journal of the American Institute of Metals, 1914.

³ It may be noted that since the samples taken for analysis were chosen mainly from those having a low melting point, the ratio of 6 to 35 does not express the true ratio of plugs composed of impure tin to the total number examined (100).

^{3401°----3}

By this is meant that, although alloys of tin and zinc can be made in all proportions, the zinc is not in the solid state dissolved in the tin forming a solid solution of homogeneous macro- and micro-

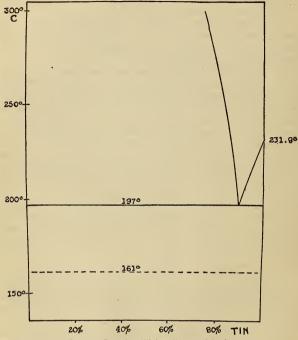


Fig. 20.—Part of equilibrium diagram of tin-zinc

structure. A slowly cooled alloy—tin 99 per cent and zinc 1 per cent—has the eutectic structure shown in Fig. 21, taken from a paper by Lorenz and Plumbridge,4 in which the eutectic

⁴ Z. Anorg. Chem., 83, p. 283; 1913.

crystallites of zinc (dark) can be seen distributed in the tin matrix. Upon long heating just under the eutectic horizontal at about 197° C the tin and zinc crystals coalesce, the eutectic disappears, and the structure attained is that shown in Fig. 23. This will be shown in experiments described below. In this alloy the tin crystals are surrounded by an envelope of zinc.

If, now, this alloy be brought in contact with a corrosive aqueous solution, the latter will attack the zinc first, eating its way into the plug through the grain or crystal interstices, and the tin filling finally becomes honeycombed in structure. The corrosion of the tin itself may now start from these intercrystalline canals, and the oxidation products remain, forming gradually the oxide network structure already referred to.

There is much analogy of the oxidation of this kind to that produced in Muntz metal sheathing upon exposure on a ship's bottom to salt water. Muntz metal (60 per cent copper and 40 per cent zinc) has a heterogeneous structure, and consists of two structural constituents or phases, the alpha and the beta solid solutions, respectively, the latter containing more zinc than the former. Upon exposure to salt water, material of this sort afterwards becomes so brittle that it can be crumbled up by hand. Examination shows that the salt water has attacked the beta constituent and has removed much of it, eating its way thus into the interior of the metallic mass, such that the metal consists of the original structural "framework" of alpha, throughout which the beta filling has been at least partially removed.

Naturally, if the water, in this case the boiler water, attacks neither the tin nor perhaps even the zinc, a plug which contains zinc may remain sound after months of service. It may be mentioned here that alkaline waters, such as would be produced by overaddition of soda boiler-water softener, attack zinc even at ordinary temperatures and probably corrode both zinc and tin at higher temperatures. Furthermore, the temperature of the water and plug will determine to a great extent the velocity of the progress made by the oxidation. At a higher temperature the corrosive action will be in general greater, the velocity of the

coalescence of the zinc eutectic will be greater, and what is more important, if the temperature rise above 197°C (about 205 pounds per square inch pressure), melting will take place at the boundary of the zinc and tin, the pressure inside will force the melted portions toward the fire end of the plug, thus leaving channels open for the entrance of the water from the water side. That the fillings of plugs do so travel in their casings from the water to fire end is shown in the case of plugs under class 3.

It is thus easily seen why it is that although no plugs have been found showing the network type of oxidation, which do not contain zinc, several have been found (see above table) which do contain zinc and which have nevertheless remained sound in service during from 3 to 12 months.

In the latter cases, the tin surface on the water side was found to be clean, proving that the boiler water used did not attack it, whereas in other plugs, and particularly in those in which network oxidation had taken place, the water-side surface of the tin was badly corroded. The normal pressure used in the boilers may also have been less in these cases. There is, however, also some significance in the fact that all five of the plugs showing this type of failure came from the same manufacturer. The explanation of this fact is to be sought in the simultaneous presence of zinc and absence of lead in the fillings of these plugs. This manufacturer happened to be using impure tin which, unlike most of the impure tin used by other manufacturers, contained no lead. The action of the lead in this respect is discussed below.

The formation of incrustation in plugs under 5 (b) is more puzzling. That this incrustation is not always entirely formed by natural means is shown, however, by the fact that analysis of it showed it to be about 96 per cent $CaSO_4$. $\frac{1}{12}$ $\frac{1}{12}$ $\frac{1}{12}$ and $CaSO_4$ was also found in plugs Nos. 1047, 1045, and 9. Since this is at the fire end, with no communication with the boiler water, the inference is that when the plug began to leak plaster of Paris was put in at the fire end to stop the leak. However, in other cases the incrustation is free from calcium and is tin oxide with traces of copper, zinc, and tin oxides containing always sulphates—usually as copper sulphate—and was probably formed by natural processes.

It is to be noticed that the tin in plugs which have oxidized in this manner is either from its melting point or analysis seen to be impure. The presence of sulphate shows that flue gases with sulphur dioxide and oxygen content have been instrumental in oxidizing the tin filling.

The explanation why some plugs containing tin fillings (see Table 2) merely melt out at the fire end leaving no oxide, and why in others the tin oxidizes and remains as oxide, is to be sought probably in the variation in operating conditions of the boilers, in variations in the kind of coal used, as, for example, in the sulphur content of the coal; also, very possibly in the devices used by the engineers in charge of boilers to stop up leaky plugs. It is possible that if plugs could be made which would not leak, this kind of deterioration would be largely eliminated.

5. TESTING OF THEORY BY SERVICE TESTS AT BUREAU

It was thought advisable to subject a number of the new plugs as well as plugs made up at the Bureau, containing definite amounts of impurities, to the action of water at high temperatures to determine what would be their behavior under these known conditions. For this purpose the plugs were put in a copper autoclave and heated for various periods at a temperature of from 180° to 195° C (350° to 380° F), in either tap or distilled water. In two cases the temperature went too high and some of the plugs of lower melting point fused. Half of each plug was heated and half saved for comparison in each case.

Of 40 new plugs heated for 195 hours, and 20 new plugs, for 140 hours in tap water, only 3 showed any change whatever—Nos. 185, 186, and 187, all from manufacturer S. These will be seen from the table above to contain lead in varying amounts. After this treatment all were somewhat distorted and covered with spongy "eruptions," illustrated in Fig. 22 of No. 185. Whereas no lead could be detected in the microstructure before heating, owing to the fineness of its distribution, after this heating the lead had coalesced as an enveloping boundary to the tin crystals. (See Fig. 23.) The plug filling was apparently only superficially oxidized.

Plugs were then made up at the Bureau of pure Banka tin, Straits tin, and Straits tin containing the following amounts of zinc and lead:

Zinc	Lead
Per cent	Per cent
0.5	
2.0	
5.0	
10.0	
	0.5
	5.0
0.5	1.0
2.0	1.0
5.0	1.0
0.5	5.0

These metals were melted in a fire-clay crucible in a gas furnace and poured into casings made of 1-inch brass tubing threaded on the inside. They were cast in pairs. Of each composition the first plug was poured with care taken to avoid oxidation, and the consequent contamination of the tin of the plug with oxide. After this was poured, air was forced through the melt for from three to five minutes, thoroughly oxidizing it, after which it was then poured into the second casing, effort being made in this case to introduce oxide into the filling of the plug. It was desired to determine whether the presence of oxide from the pouring aided the process of oxidation in service. It is interesting to notice that even in one of the plugs in which the oxide must have been present to the extent of about 25 per cent, it could be detected only microscopically in the structure of a polished section. No coarse macroscopic oxide structures could be produced resembling those produced in service and described above.

Some of these were then heated in tap and some in distilled water for about 500 hours at from 180° to 195° C (350° to 380° F). There seemed to be no difference in the action of distilled and the tap water on the plugs.

After heating, the plugs containing zinc or lead in amounts equal to or above 0.5 per cent were usually found cracked. Indeed, in the case of the plug filling with 10 per cent zinc, an almost perfect

inverted pyramid had cracked off and had been forced up several millimeters. This half plug is shown in Fig. 24. This is doubtless due to the stresses caused by the expansion between the tin crystals of tin-zinc eutectoid during its melting which begins at about 197° C (385° F). In some cases, particularly when lead was present, the filling had become porous, due to the melting out of the low melting eutectoid which in this case melts around 170° C (330° F).

No change could be detected in the samples of Banka and Straits tin caused by this treatment other than a sight surface oxidation.

Every plug which contained zinc and no lead showed a network structure after 500 hours in the autoclave. This is shown in Fig. 25, of a plug containing 0.5 per cent zinc. This network structure was the more pronounced the higher the zinc content and was in many cases better developed near the surface than inside. Fig. 25 shows the structure of this plug after grinding off about 0.5 mm. This plug was sawed in two and an inside surface polished. The structure of this surface, which was about 5 to 10 mm. from the water during the heating period, is shown in Fig. 26.

It appears, then, that even with ordinary tap water some oxidation of this type takes place, for if none had taken place the network structure developed by the coalescence of the zinc should have had approximately the same density throughout, which is clearly not the case, as shown in this plug.

The structure of those plugs which contained zinc and lead, after heating with distilled water, showed a much less developed network structure than those containing the same amount of zinc and no lead under the same conditions.

It was shown here and during the examination of plugs whch had been in service for periods of from 4 to 12 months, and had remained sound, that tin may contain zinc, and be heated to temperatures around 180° C or 350° F (corresponding to an average boiler pressure of 150 pounds per square inch) and still not develop the coarse coalesced "network" structure described above. This may have been partly due to the fact that the temperatures to which they were exposed were lower than those to which the plugs

of class 5 (a), together with those heated at the Bureau, had been exposed; but there is little doubt but that lead partially, at least, prevents the formation of this coarse "network" structure in tin containing zinc. This is shown by the fact that—

- 1. Four plugs (class 5, a) contained zinc and no lead, and had developed this structure.
- 2. Tin samples with zinc and no lead developed upon heating a much more pronounced network structure than those containing the same amount of zinc and 1 per cent lead. This is shown in Figs. 27 and 28 of specimens with 2 per cent zinc and no lead, and with 2 per cent zinc and 1 per cent lead, respectively.
- 3. Plugs containing zinc and lead, and which had been in service for periods of from 4 to 12 months did not develop this structure; indeed, in most cases neither the zinc nor the lead could be detected with certainty in their microstructure. This was true, for example, of plug No. 1035, containing 1.8 per cent zinc and 0.1 per cent of lead, which had been in service 3 months and was still absolutely sound.

It seems then that the progress of the "network" oxidation is dependent upon the previous presence of the coalesced network zinc-tin structure, and if for some reason the zinc is present in another form of distribution the oxidation can not proceed in this manner.

Upon heating with water in the autoclave no difference could be noticed in the behavior of the sound, i. e., unoxidized, and the plugs oxidized before pouring.

III. TESTING OF THE PURITY OF TIN

It is suggested that the use of a high-grade tin of the purity of Banka, Straits, Pyrmont, or Williams, Harvey & Co., refined (see analyses by Cowan, Appendix 1), would eliminate the danger of deterioration by oxidation of the fillings of tin plugs. Of these varieties, Banka is undoubtedly the most consistently pure, although some samples of other varieties were of almost equal purity—for example, Williams, Harvey & Co., refined. It would seem safest, therefore, to require a tin in such plugs to be 99.9 per cent pure and to contain less than 0.01 per cent each of zinc

and lead. This would admit Banka tin and some lots of other varieties. It has, however, been in the past year impossible at times to obtain Banka tin on the market. For such a contingency provision must be made for admitting other and slightly poorer tins. If the specifications called for tin of 99.8 per cent purity, containing less than 0.05 per cent lead and less than 0.01 per cent zinc, most of the high-grade tins would be included, and such tin, with the higher lead content, would probably be as safe for use in plugs as the former, as there is as yet no evidence that a lead content of even 0.1 per cent is harmful in such plugs.

Frequent tests by chemical analysis must be made of the purity of the tin bought under such specifications as those recommended above. It can be seen from Table 2 that such analysis may be limited in most cases to a determination of zinc and lead, which seem to be the principal impurities.

A somewhat quicker method of determining whether or not a tin sample is pure is given in the determination of its melting point. Table 3 is given below, in which the lowering of the melting point of tin for 1 per cent of various ordinary metallic impurities has been calculated from the results of thermal analysis of these alloys by various investigators (see Bornemann, 1909–1912). The rough assumption has been made in these calculations that the liquidus curve is linear.

TABLE 3
Effect of Impurities on Melting Point of Tin

Metal	Tin con- taining—	Melting point	Lowering of melting point per i per cent of metal calculated
	Per cent	°c	°c
Antimony	7.5	240	+ 1.0
Bismuth	5.5	225	- 1.2
Iron	2.0	300	+30.0
Lead	2.5	225	- 2.8
Zinc	3.0	225	- 2.3

It is seen that small amounts of impurities may in general be readily detected although the simultaneous presence of metals, such as antimony and zinc, in proper amounts might give an alloy having a melting point equal to that of pure tin. In the samples analyzed the only impurities found in appreciable amounts were zinc and lead, each of which lowers the melting point. Therefore the determination of the melting or freezing point of the tin may be accepted as a useful and rapid test of its purity. It may be noted that extremely small amounts of lead and zinc of the order of magnitude of 0.02 or 0.03 per cent can not be detected by such

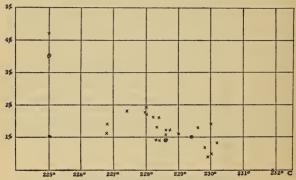


Fig. 29.—Effect of small quantities of lead and zinc upon freezing point of tin

a thermal method and it is also not possible to distinguish with certainty between "Kahlbaum," Banka, and Straits tin by the ordinary determination of the melting point as made by the cooling curve method.

In Fig. 29 are plotted the melting points of all of the tin specimens analyzed, as a function of the percentage of the two impurities, lead and zinc. In order to avoid using three coordinates, it was roughly assumed, from the table above, that I per cent lead was equal in effect to I.I per cent zinc and the sum of the zinc content and of the lead content multiplied by I.I was plotted as ordinates. This is equivalent to assuming that the effects of zinc and lead

upon the lowering of the freezing point of tin are additive, or that the ternary liquidus surface for small lead and zinc contents is formed by the motion of a straight line. From this curve an approximate estimate may be made of the amount of combined zinc and lead in a tin which contains these two impurities only.

IV. CONCLUSIONS

The fact that stands out most strongly throughout this investigation is that zinc should not be present in the tin fillings of fusible plugs. The lowest zinc content actually found in any of the four plugs analyzed, which displayed the "network" type of oxidation. was 0.3 per cent, but this can not be accepted as the actual lowest value of the zinc content at which oxidation can take place. Furthermore, although zinc is, because of its greater corrodability, most dangerous when coalesced into a network structure such as is developed upon heating at about 180°, other metals which do not form solid solution with tin may also cause the formation of this structure, as, for instance, lead. It seems then that in such plugs tin must be used which is as free as possible from zinc and lead. This statement is made notwithstanding the apparent fact that if zinc is present a small content of lead is actually beneficial; it appears better, however, to prevent this oxidation by using pure tin rather than by adding lead in case the tin already contains zinc.

A consideration of the results of the tin analyses by Cowan, given in Appendix 1, shows that it is possible to get Banka and other tin which contains only traces of zinc and at the utmost 0.010 per cent of lead. It is highly probable that the use of tin of such purity would eliminate the danger of oxidation of the "network" type.

With the exception of plug No. 122, which had a melting point of 231.9° C, and in which the formation of nonmetallic inclosures had not proceeded by natural means, as shown above, the plugs of the 5 (b) class (i. e., with inclusions of solid oxide at the fire end) all contained impurities, probably to the extent of about I to 1.5 per cent. The inference is, therefore, that oxidation of the tin in service would cease with the introduction of the use

of a tin of purity equal to that of Banka, probably also of tin of purity equal to that of Straits or Pyrmont. Observations are made above regarding the testing of the purity of tin.

However, one question may be raised. A leaky plug will always be a temptation to careless practice on the part of the engineer in charge. He may stop them up instead of replacing them. Now, the chances that leaks may develop in a plug are fairly large. The coefficient of expansion per degree centigrade of the material of a casing will be around 0.000020, whereas that of tin is about 0.000023. Tin undergoes an allotropic change at about 160° C, accompanied by a change of volume of about 0.03 per cent. Therefore, opportunity is constantly given for interplay between plug filling and casing during temperature changes. A number of plugs which had been in service were removed because of leaking.

Considering now the three sets of specifications (Appendixes 2 and 3), it is seen that any set of specifications such as those of the Interstate Commerce Commission, which totally ignore the question of the purity of the tin, are insufficient. The specifications of the American Society of Mechanical Engineers seem to limit the quality of the tin in calling for tin of a melting point between 400° and 500° F, but in reality this specification has no significance from the standpoint of the purity of the tin, since it would admit tin containing as much as 65 per cent of lead or 15 per cent of zinc. Manifestly such a specification is worthless. The Steamboat Inspection Service requires at present "Banka tin," but propose to amend this paragraph to call for "tin 99.7 per cent pure, containing not more than o.1 per cent of lead and not more than o.1 per cent of zinc." The latter is doubtless a more practical specification than the former, but there is no doubt but that better tin than this can and should be obtained for such plugs, as shown in Section III.

The requirement of the Interstate Commerce Commission that fusible plugs "be removed and cleaned of scale once every month" is desirable, since, as above demonstrated, an impure plug may begin to show visible signs of deterioration after only 500 hours' service. A combination of test of purity of new plugs from each heat cast with frequent inspections or discarding of plugs would appear to be the safest practice.

In view of the fact that many manufacturers are not furnishing pure tin for fusible boiler plugs, and it having been shown above that impure tin may be dangerous, it would probably be desirable, in the interests of safety, to license a few manufacturers whose product could be rigidly controlled by Federal inspection.

1. SUMMARY

- 1. An explanation has been sought for the "failure" by oxidation of fusible tin boiler plugs during service. These failures are of two types—(a) those in which the oxide forms as an interlocking "network" throughout the tin of the filling; (b) those in which the oxide forms as a solid hard mass at the fire end of the plug.
- 2. About 950 new and 100 used plugs were examined, the latter classified according to the type of change or deterioration which had taken place in them during service, and a number were tested for purity of the tin, both by determination of the melting point of the latter, and by chemical analysis. Lead and zinc were found to be the principal impurities present.
- 3. An explanation for the formation of the "network" type of oxidation is found in the presence of zinc in amounts varying from 0.3 to 4 per cent.
- 4. The conclusion is drawn that, since all plugs examined, which were "dangerous," contained impurities, the use of pure tin of the quality of Banka, of Williams, Harvey & Co., refined, or even of Straits or Pyrmont (see Appendix 1) would probably eliminate the danger of oxidation of these plugs in service.
- 5. The relation of these findings to existing specifications for fusible plugs is discussed and more rigorous inspection of the product of licensed manufacturers suggested.
- A. B. Lort, of the chemical division, made all of the quantitative and most of the qualitative chemical analyses for this investigation, and to him, as well as to R. W. Woodward, R. G. Waltenberg, C. P. Karr, and A. S. McCabe, for their aid in this work, the authors' thanks and appreciation are here expressed.

The material for this investigation was furnished by the Steamboat Inspection Service, as noted above.

Washington, May 28, 1915.

APPENDIXES

APPENDIX 1 .- ANALYSES OF PIG TIN BY COWAN

Analyses are here given of series of brands of tin by W. A. Cowan (Journal of the American Institute of Metals, 1914).

Comparison-Pig Tin Analyses

[A=American Sheet & Tin Plate Co.; B=Ledoux & Co.; C=A. H. Knight; D=National Lead Co.]

BANKA

		_	r /	
	A	В	С	D
	Per cent	Per cent	Per cent	Per cent
Lead	Trace	0.010	Trace	Trace
Arsenic	0.024	0.004	Trace	None
Antimony	0.038	None	0.006	0.006
Copper	0.003	- 0.009	0.002	0.004
Cadmium		None		None
Bismuth		0.002	Nil	None
Iron	Trace	0.004	0.023	0.019
Zinc	Trace			Trace
Ni and Co		None	Nil	None
Manganese		None		None
Tungsten				None
Sulphur	Trace		Trace	Trace
Phosphorus	Trace	None	Nil	0.008
Tin	a 99. 935	a 99. 971	99.963	a 99. 963
Total	100.000	100.000	99. 994	100.000

STRAITS

Lead.	0. 057	0.080	0.049	0.064
Arsenic		0.072	0.058	0.077
Antimony	0. 103	None	0.018	0.018
Copper	0.013	0. 027	0.020	0.020
Cadmium		None		None
Bismuth		0.003	0.004	None
Iron	Trace	0.005	0.003	0.005
Zinc	Trace			0.015
Ni and Co		None	Nil	None
Manganese		None		None
Tungsten				None
Sulphur	Trace		Trace	0.009
Phosphorus	Trace	None	Nil	0.010
Tin	a 99. 743	a 99. 813	99.831	a 99. 782
Total	100.000	100.000	99. 983	100.000



Fig. 2.—Original plug showing tin (light) and tin oxide. Magnification = 1/2



Fig. 3.—Used plug with filling partially melted out. Magnification =½



Fig. 4.—Used plug with filling partially melted out. Magnification = ½



Fig. 5.—Used plug showing swelled filling. Magnification $=\frac{1}{2}$



Fig. 6.—Used plug showing swelled filling. Magnification = 1/2



Fig. 7.—Used plug showing oxide layer between filling and casing. Magnification =½



Fig. 8.—Used plug. Magnification = ½



Fig. 9.—Used plug showing network type of oxidation. Magnification = 1/2



Fig. 10.—Used plug showing network type of oxidation.

Magnification = 1/2



Fig. 11.—Used plug showing network type of oxidation. Magnification = I



FIG. 12.—Used plug showing network type of oxidation. Magnification $=\frac{1}{2}$



Fig. 13.—Used plug, showing network type of oxidation. Magnification = 1



Fig. 14.—Used plug showing solid "oxide" inclusions at fire end. Magnification = 1/2



Fig. 15.—Used plug showing solid "oxide" inclusions at fire end. Magnification = \frac{1}{2}



Fig. 16.—Used plug showing solid "oxide" inclusions at fire end. Magnification = ½



Fig. 17.—Used plug showing solid "oxide" inclusions at fire end. Magnification = ½



FIG. 18.—Used plug showing solid "oxide" inclusions at fire end. Magnification = 1/2



Fig. 19.—Used plug. Magnification $=\frac{1}{2}$



FIG. 21.—Structure of zinc-tin alloy with I per cent zinc, slowly cooled. Magnification=Ioo, reduced to 45 in printing



Fig. 22.—Shows the two halves of a plug containing lead; the left half is as received (unused), the right half has been treated in water under pressure at about 180° C. Magnification = \(\frac{1}{2} \)



Fig. 23.—This photomicrograph shows microstructure of heated half of plug shown in Fig. 22. Magnification =20, reduced to 9 in printing



FIG. 24.—This half plug has cracked as shown upon heating with water at 180° C. The plug contains zinc. Magnification = 1/2

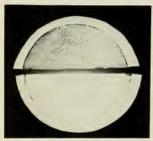


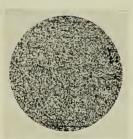
Fig. 25.—Two halves of a plug containing 0.5 per cent zinc. The upper half has been headed for 500 hours from 180° to 105° C; the lower half is as received. Magnification=1



Fig. 26.—Same as Fig. 25; center section of the heated half



Fig. 27.—Photomicrograph shows structure of plug containing 2 per cent sinc and no lead after treating with water in autoclave for 500 hours at about 180°C. Magnification =15, reduced to 7 in printing



F16. 28.—Photomicrograph shows structure of plug containing 2 per cent zinc and 1 per cent lead, heated as in Fig. 27. Magnification =15, reduced to 7 in printing



PYRMONT (AUSTRALIAN)

	A	В	С	D
	Per cent	Per cent	Per cent	Per cent
Lead	0.019	0.045	0.016	0.045
Arsenic	0.020	0.035	0.019	0.038
Antimony	0.054	0.074	0.051	0.098
Copper	0.023	0.027	0.015	0.024
Cadmium		None		None
Bismuth		0.010	0.007	None
Iron	Trace	0.003	0.003	0.003
Zinc	Trace			0.010
Ni and Co		None	Nil	None
Manganese		None		None
Tungsten				None
Sulphur	Trace		Trace	Trace
Phosphorus		None	Nil	0,020
Tin	a 99.784	a 99. 806	a 99. 866	a 99. 762
Total	100.000	100.000	99.977	100.000

WILLIAMS, HARVEY & COMPANY (ENGLISH)

		Com	Refined			
	. A	В	С	D	С	D
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Lead	0.339	0.374	0.380	0.387	Trace	0.01
Arsenic	.038	.078	.060	.077	0.049	.06
Antimony	.336	. 220	.215	-252	.032	.03
Copper	.075	.100	-060	. 090	.015	.01
Cadmium		None		None		Non
Bismuth		.070	. 059	. 064	.002	Non
ron	Trace	.008	.004	. 002	Trace	.00
linc	Trace			.006		. 01
Ni and Co		None	.007	None	Nil	Non
Manganese		None		None		Non
Cungsten				None		Non
Sulphur	Trace		.002	.006	Trace	Trac
Phosphorus	Trace	None	Trace	-007	Nil	Trac
Pin	a 99. 212	a 99.150	99.260	a 99.109	99. 920	a 99.86
Total	100.000	100-000	100-047	100.000	100.018	100.00

a By difference.

APPENDIX 2. EXISTING SPECIFICATIONS FOR FUSIBLE TIN BOILER PLUGS

At their annual meeting, January to March, 1915, the board of supervising inspectors, Steamboat-Inspection Service, proposed the following specifications to supersede those already in force, adopted in December, 1914:⁵

FUSIBLE PLUGS

SECTION 20, ocean and coastwise; lakes, bays, and sounds; and rivers. (Amended.)

20. Fusible plugs for use in boilers of steam vessels under the jurisdiction of the Steamboat-Inspection Service shall be madeof a bronze casing with the bore tapering continuously and evenly from end to end, and filled from end to end with [good, pure Banka] tin [with a continuous taper from end to end of filling. The bore of the plug may be lightly threaded for a part or all of its length if deemed necessary to retain the filling in the plug under pressure, but no counterbore, recess, or cavity other than a thread will be allowed] not less than 90.7 per cent pure and to contain not more than 0.1 per cent of lead and not more than 0.1 per cent of lead and not more than 0.1 per cent of lead and not more than one thirty-second of an inch in depth and width, but no recess, thread, or cavity other than this countersink shall be allowed.

Fusible plugs, except those which are hereafter provided for, shall have an external diameter of not less than three-fourths of an inch pipe tap, and the [Banka tin] filling shall be at least one-half of an inch in diameter at the smaller end, and shall have a larger diameter at the opposite end of the plug: Provided, however, That all fusible plugs fitted in boilers carrying a steam pressure exceeding 150 pounds to the square inch may be reduced at the smaller end of the [Banka tin] filling to five-sixteenths of an inch in diameter.

Every boiler other than boilers of the water-tube type shall be fitted with at least two fusible plugs as described above, and located as follows:

Upright boilers shall be fitted with two fusible plugs of an external diameter of not less than three-eighths of an inch pipe tap, the [Banka tin] filling to be at least one-fourth of an inch in diameter at the smaller end and shall have a greater diameter at the opposite end. The fusible plugs shall be located in separate tubes not more than 2 inches below the lowest gauge cock [, but in such boilers having a cone top the plugs shall be inserted in the upper sheet].

Externally heated cylindrical boilers, with flues, shall have one plug in the top of the upper flue, not more than 4 feet from the back end of the flue, and shall also have a plug fitted to the shell of the boiler immediately below the fire line and not less than 4 feet from the front end: Provided, however, That when the flues are not more than 6 inches in diameter fusible plugs of not less diameter than three-eighths of an inch pipe tap may be used in such flues.

Fire box, scotch, and other types of shell boilers not specially provided for, having a combustion chamber common to all furnaces, shall have two plugs fitted to the crown sheet and not more than 12 inches apart. Boilers fitted with separate combustion

⁶ The parts of the rules struck out are inclosed in brackets [thus], while the addition to the rules are printed in *italic*.

chambers shall be fitted with a fusible plug in the center of the crown sheet of each chamber.

Boilers of types not herein provided for shall be fitted with at least two fusible plugs of such dimensions and located in such parts of the boiler as will, in the judgment of the local inspectors, best meet the purposes for which they are intended.

Fusible plugs shall be renewed after six months of service, and the inspector of boilers shall assure himself at each annual inspection by personal examination and by testing the ends of the filling by filing to determine its condition that the plugs are in good and serviceable condition.

Fusible plugs shall be so fitted that the smaller end of the [Banka tin] filling is exposed to the fire, and shall be at least r inch higher on the water side than the plate or flue in which they are fitted.

Notwithstanding anything which may be contained in this rule, fusible plugs shall be so fitted that the end of the [Banka tin] filling on the water end of the plug is not less than x inch above the dangerous low-water level.

Manufacturers of fusible plugs shall stamp their name or initials thereon for identification and shall file with the Supervising Inspector General of the Steamboat-Inspection Service at Washington, D. C., a certificate duly sworn to that such plugs are filled with [good, pure Banka] tin [free from scoriae or oxides] of the character required by this rule and made in accordance [with this rule] therewith, and shall also furnish him a sample plug for each lot of [50] 100 plugs or less and a proportionate number of samples for larger lots [, such sample plugs to be split evenly from end to end so that the construction may be observed].

Each manufacturer of fusible plugs shall number all plugs in accordance with the number of the heat from which the plugs were filled. For instance, the first pouring shall be number one, and all plugs filled from this heat shall be numbered 1; the next pouring shall be numbered 2, etc. The samples furnished the Supervising Inspector General shall bear the same number for any one heat and shall be part of the heat from which the plugs represented by the sample are poured.

The heat number shall be plainly stamped on each end of filling with numbers not less than one-twelfth inch in height.

The manufacturer's name or initials shall be plainly stamped on the larger end or face of the casing.

One sample plug shall be furnished from each heat of [50] 200 plugs or less. For [over 50] more than 100 and not [over 100] more than 200 plugs of any one heat, two plugs shall be furnished, etc. Such sample plugs shall not be split as formerly required.

In transmitting samples of fusible plugs to the Supervising Inspector General, the fusible plugs and the letters of transmittal shall be addressed as follows: "Supervising Inspector General, Steamboat-Inspection Service, Department of Commerce, Washington, D. C."

One letter of transmittal shall be required for each heat.

In letter of transmittal the following information shall be stated:

Number of heat.

Number of fusible plugs manufactured from the heat.

Number of samples of fusible plugs from the heat transmitted.

Name of manufacturer or initials stamped on casing of plug.

Following is a general form of affidavit to be followed by manufacturers of fusible plugs:

STATE OF ——, County of ——.

I hereby certify, on this —— day of ———, 191—, that I am ————, of the (State owner or name position.) manufactory of ———, located at ———, in the State of ————; that all fusible plugaturnished for use in boilers of steam vessels under the jurisdiction of the Steamboat-Inspection Service by the said manufactory will be filled with [good, pure Banka] tin [free from scoriæ or oxides] of the character required, and will be made in accordance with the rules and regulations of the Board of Supervising Inspectors, Steamboat-Inspection Service, governing the manufacture of fusible plugs; and that I am authorized to make this certificate.

Subscribed and — to before me this — day of —, 191—.

[NOTARY'S SEAL.] (Signature)

Notary Public.

The certificate shall be executed by some person having authority to make the statements contained therein.

The affidavit shall be sent to the Supervising Inspector General.

On receipt of a properly executed affidavit by the Supervising Inspector General, the inspectors of the Steamboat-Inspection Service and the merchant marine generally shall be notified.

In their final report to the American Society of Mechanical Engineers, published in February, 1915, the boiler-code committee included the following specifications for fusible plugs among their "Standard specifications."

REPORT OF THE COMMITTEE TO FORMULATE STANDARD SPECIFICATIONS FOR THE CONSTRUCTION OF STEAM BOILERS AND OTHER PRESSURE VESSELS AND FOR CARE OF SAME IN SERVICE.

FUSIBLE PLUGS.

- 428. Fusible plugs, if used, shall be filled with tin with a melting point between 400 and 500 degrees Fahrenheit.
- 429. The least diameter of fusible metal shall be not less than one-half inch, except for maximum allowable working pressures of over 175 pounds per square inch or when it is necessary to place a fusible plug in a tube, in which case the least diameter of fusible metal shall be not less than three-eighths inch.
 - 430. Each boiler may have one or more fusible plugs, located as follows:
- (a) In horizontal return tubular boilers: In the rear head, not less than z inches above the upper row of tubes, the measurement to be taken from the line of the upper surface of tubes to the center of the plug, and projecting through the sheet not less than z inch.
- (b) In horizontal flue boilers: In the rear head, on a line with the highest part of the boiler exposed to the products of combustion, and projecting through the sheet not less than r inch.

- (c) In traction, portable, or stationary boilers of the locomotive type or star water tube boilers: In the highest part of the crown sheet, and projecting through the sheet not less than x inch.
- (d) In vertical fire-tube boilers: In an outside tube, not less than one-third the length of the tube above the lower tube sheet, and projecting through the sheet not less than x inch.
- (e) In vertical fire-tube boilers, Corliss type: In a tube, not less than one-third the length of the tube above the lower tube sheet.
 - (f) In vertical submerged tube boilers: In the upper tube sheet.
- (g) In water-tube boilers, horizontal drums, Babcock & Wilcox type: In the upper drum, not less than 6 inches above the bottom of the drum, over the first pass of the products of combustion, and projecting through the sheet not less than 1 inch.
- (h) In Stirling boilers, standard type: In the front side of the middle drum, not less than 4 inches above the bottom of the drum, and projecting through the sheet not less than 1 inch.
- (i) In Stirling boilers, superheater type: In the front drum, not less than 6 inches, above the bottom of the drum, exposed to the products of combustion, and projecting through the sheet not less than 1 inch.
- (j) In water-tube boilers, Heine type: In the front course of the drum, not less than 6 inches above the bottom of the drum, and projecting through the sheet not less than 1 inch.
- (k) In Robb-Mumford boilers, standard type: In the bottom of the steam and water drum, 24 inches from the center of the rear neck, and projecting through the sheet not less than x inch.
- (1) In water-tube boilers, Almy type: In a tube or fitting exposed to the products of combustion.
- (m) In vertical boilers, Climax or Hazelton type: In a tube or center drum not less than one-half the height of the shell, measuring from the lowest circumferential seam.
- (n) In Cahall vertical water-tube boilers: In the inner sheet of the top drum, not less than 6 inches above the upper tube sheet, and projecting through the sheet not less than r inch.
- (o) In Wickes vertical water-tube boilers: In the shell of the top drum and not less than 6 inches above the upper tube sheet, and projecting through the sheet not less than 1 inch; so located as to be at the front of the boiler and exposed to the first pass of the products of combustion.
- (b) In Scotch-marine type boilers: In the combustion chamber top, and projecting through the sheet not less than r inch.
- (q) In dry back Scotch type boilers: In the rear head, not less than 2 inches above the upper row of tubes, and projecting through the sheet not less than 1 inch.
 - (r) In economic type boilers: In the rear head, above the upper row of tubes.
- (s) In cast-iron sectional-heating boilers: In a section over and in direct contact with the products of combustion in the primary combustion chamber.
- (t) In water-tube boilers, Worthington type: In the front side of the steam and water drum, not less than 4 inches above the bottom of the drum, and projecting through the sheet not less than 1 inch.
- (u) For other types and new designs, fusible plugs shall be placed at the lowest permissible water level, in the direct path of the products of combustion, as near the primary combustion chamber as possible.

In the "Rules and Instructions for Inspection and Testing of Locomotive Boilers and Their Appurtenances" of the division of locomotive boiler inspection of the Interstate Commerce Commission there is found the following paragraph relating to fusible plugs:

14. If boilers are equipped with fusible plugs they shall be removed and cleaned of scale at least once every month.

APPENDIX 3

DEPARTMENT OF COMMERCE, STEAMBOAT-INSPECTION SERVICE.

General Rules and Regulations prescribed by the Board of Supervising Inspectors, amended January, 1913, and further amended by action of executive committee of the Board of Supervising Inspectors, meetings April 18, July 9, August 16, October 21, and December 10, 1913. (Amendments approved by the Secretary of Commerce. Edition of January 13, 1914.)

FUSIBLE PLUGS.

21. Every boiler, other than boilers of the water-tube type, shall have at least one fusible plug as described below. Plugs shall be made of a bronze casing filled with good Banka tin tapering straight from end to end of filling. The manufacturers of fusible plugs shall stamp their name or initials thereon for identification, and shall file with the local inspectors a certificate, duly sworn to, that such plugs are filled with Banka tin and made in accordance with this rule.

Fusible plugs, except as otherwise provided for, shall have an external diameter of not less than three-fourths of an inch pipe tap, and the Banka tin shall be at least one-half of an inch in diameter at the smaller end and shall have a larger diameter at the opposite end of the plug: Provided, however, That all plugs used in boilers carrying a steam pressure exceeding 150 pounds to the square inch may be reduced at the smaller end of the Banka tin to five-sixteenths of an inch in diameter.

Fusible plugs, when used in the tube of upright boilers, shall have an external diameter of not less than three-eighths of an inch pipe tap, and the Banka tin shall be at least one-fourth of an inch in diameter at the smaller end and shall have a greater diameter at the opposite end of the plug.

Externally heated cylindrical boilers, with flues, shall have one plug inserted in one flue, and also one plug inserted in shell of each boiler immediately below the fire line and not less than 4 feet from the front end: Provided, however, That when such flues are not more than 6 inches in diameter, a fusible plug of not less diameter than three-eighths-inch pipe tap may be used in such flues.

Other shell boilers, except especially provided for, shall have one plug inserted in the crown sheet of the back connection.

Vertical tubular boilers shall have one plug inserted in one of the tubes at least 2 inches below the lowest gauge cock, but in boilers having a cone top the plug shall be inserted in the upper tube sheet.

All plugs shall be inserted so that the small end of the Banka tin shall be exposed to the fire.

It shall be the duty of the inspector at each annual inspection to see that the plugs are in good condition. (Sec. 4418, R. S.)

DEPARTMENT OF COMMERCE. STEAMBOAT-INSPECTION SERVICE, Washington, June 30, 1914.

CIRCULAR LETTER.

United States Supervising and Local Inspectors, Steamboat-Inspection Service, Manufacturers of Fusible Plugs,

Owners of Steam Vessels, and others concerned:

Under the provisions of section 4405, Revised Statutes of the United States, as amended by the act of Congress approved February 8, 1907, the executive committee of the Board of Supervising Inspectors, Steamboat-Inspection Service, at a meeting held in New York, N. Y., on June 22, 1914, adopted the following resolution:

Resolved, That section 21, Rule II, page 44, of the General Rules and Regulations prescribed by the Board of Supervising Inspectors, as amended January, 1913, edition of January 13, 1914, be struck out and the following substituted therefor:

FUSIBLE PLUGS.

21. Fusible plugs for use in boilers of steam vessels under the jurisdiction of the Steamboat-Inspection Service shall be made of a bronze casing filled with good, pure Banka th tapering evenly from end to end of filling.

Fusible plugs, except those which are hereafter provided for, shall have an external diameter of not less than three-fourths of an inch pipe tap, and the Banka tin filling shall be at least one-half of an inch in diameter at the smaller end, and shall have the state of the shall be at least one-half of an inch in diameter at the smaller end, and shall have the shall be at least one-half of an inch in diameter at the smaller end, and shall have the shall be at least one-half of an inch in diameter at the smaller end, and shall have the shall be at least one-half of an inch in diameter at the smaller end, and shall have the shall be at least one-half of an inch in diameter. larger diameter at the opposite end of the plug: Provided, however, That all fusible plugs fitted in boilers carrying a steam pressure exceeding 150 pounds to the square inch may be reduced at the smaller end of the Banka tin filling to five-sixteenths of an inch in diameter.

Every boiler other than boilers of the water-tube type shall be fitted with at least two fusible plugs, as described above, and located as follows:

Upright boilers shall be fitted with two fusible plugs of an external diameter of not less than three-eighths of an inch pipe tap, the Banka tin filling to be at least one-fourth of an inch in diameter at the smaller end and shall have a greater diameter at the opposite end. The fusible plugs shall be located in separate tubes not more than 2 inches below the lowest gauge cock, but in such boilers having a cone top the plugs shall be inserted in the upper tube sheet.

Externally heated cylindrical boilers, with flues, shall have two plugs in the top of

Externally fleated cylindras boilers, with flues, shall have two plugs in the top of the upper flue, one of the plugs to be not more than 4 feet from the back end of the flue and the other to be placed about the middle of the length of the flue, and shall also have a plug fitted to the shell of the boiler immediately below the fire line, and not less than 4 feet from the front end: Provided, however, That when the flues are not more than 6 inches in diameter fusible plugs of not less diameter than three-citable for inch pinc the court is not flue. eighths of an inch pipe tap may be used in such flues.

Fire-box, Scotch, and other types of shell boilers not specially provided for shall

have three plugs fitted to the crown sheet of the combustion chamber, one to be fitted about 12 inches inboard on each end of the crown and one in the center. Boilers fitted with separate combustion chambers shall be fitted with a fusible plug in the

center of the crown sheet of each chamber.

Boilers of types not herein provided for shall be fitted with at least two fusible plugs of such dimensions and located in such parts of the boiler as will, in the judgment of the

local inspectors, best meet the purposes for which they are intended.

Fusible plugs shall be renewed after four months of service, and the inspector of boilers must assure himself, by personal observation and by testing with a file to determine the character of the filling at each annual inspection, that they are in good condition.

Fusible plugs shall be so fitted that the smaller end of the Banka tin is exposed to the fire, and shall be at least I inch higher on the water side than the plate or flue in which they are fitted.

Notwithstanding anything which may be contained in this rule, fusible plugs shall be so fitted that the end of the Banka tin on the water end of the plug is not

less than I inch above the dangerous low-water level.

Manufacturers of fusible plugs shall stamp their name or initials thereon for identification, and shall file with the Supervising Inspector General of the Steamboat Inspection Service at Washington, D. C., a certificate duly swom to that such plugs are filled with good, pure Banka tin free from scorize or oxides, and made in accordance with this rule, and shall also furnish him a sample plug for each lot of 20 plugs or less, and a proportionate number of samples for larger lots.

This action of the executive committee received the approval of the Secretary of Commerce on June 25, 1914, under the provisions of sections 4405 and 4491, Revised Statutes, and has now the force of law.

In pursuance of the provisions of the above resolution, the following instructions are required to be observed by manufacturers of fusible plugs for use in boilers of steam vessels under the jurisdiction of the Steamboat-Inspection Service.

Each manufacturer of fusible plugs will number all plugs in accordance with the number of the heat from which the plugs were filled. For instance, the first pouring after this rule takes effect will be number one, and all plugs filled from this heat will be numbered i. The next pouring will be number two, and all the plugs filled from this heat will be numbered i, etc. The samples furnished the Supervising Inspector General must bear the same number for any one heat and must be a part of the heat from which the plugs represented by the sample are poured.

The heat number will be plainly stamped on each end of filling with numbers not less than one-twelfth inch in height.

The manufacturer's name or initials will be plainly stamped on the larger end or face of the casing.

One sample plug will be furnished from each heat of 20 plugs or less. For over 20 and not over 40 plugs or any one heat two plugs will be furnished, etc.

In transmitting samples of fusible plugs to the Supervising Inspector General, the fusible plugs and the letters of transmittal will be addressed as follows: "Supervising Inspector General, Steamboat-Inspection Service, Department of Commerce, Washington, D. C."

One letter of transmittal will be required for each heat.

In letter of transmittal the following information will be stated:

Number of heat.

Number of fusible plugs manufactured from the heat.

Number of samples of fusible plugs from the heat transmitted.

Name of manufacturer, or initials, stamped on casing of plug.

Following is a general form of affidavit to be followed by manufacturers of fusible plugs:

STATE OF ———, County of ———.	
I hereby certify, on this —— day of ——— 191—, that I am ————, of (State owner, or name position	the
(State owner, or name position)
manufactory of ——— located at ——— in the State of ———; that all fusible pl	
furnished for use in boilers of steam vessels under the jurisdiction of the Steambo	at-
Inspection Service by the said manufactory will be filled with good, pure Banka	
free from scoriæ or oxides, and will be made in accordance with the rules and re	gu-
lations of the board of supervising inspectors, Steamboat-Inspection Service, gove	
ing the manufacture of fusible plugs; and that I am authorized to make this certifica	

The certificate must be executed by some person having authority to make the statements contained therein.

The affidavit must be sent to the Supervising Inspector General.

On receipt of a properly executed affidavit by the Supervising Inspector General, the inspectors of the Steamboat-Inspection Service and the merchant marine generally will be notified.

All fusible plugs at present in stock must be refilled in accordance with the rule of the Board of Supervising Inspectors and the instructions contained herein.

The rule is effective on and after June 25, 1914.

Each board of local inspectors will furnish a copy of this circular letter to each manufacturer of fusible plugs and to each owner of steam vessels in its district.

GRO, UPLER.

Supervising Inspector General.

Approved June 30, 1914.
WILLIAM C. REDFIELD,

Secretary of Commerce.



Coali					

	(Continued live page : of cover)
\mathcal{I}_{t}	Special Studies in Electrolysis Mitigation (55 pp.)
	E, B. Rosa and Buston McCollum
28.	Methods of Making Electrolysis Surveys (pp.)
29.	Variation in Results of Sieving with Standard Cement Sieves (16 pp.)
	R. J. Wig and J. C. Pearson
30.	The Viscosity of Porcelain Bodies (9 pp.), A. V. Bleininger and Paul Teetor
3 T.	Some Leadless Boro-Silicate Glazes Maturing at about 1,100° C. (21 pp.) E. T. Montgomery
	Special Studies in Electrolysis Mitigation, No. 2. Electrolysis from
32.	Electric Railway Currents and Its Prevention—Experimental Test on a
	System of Insulated Negative Feeders in St. Louis (34 pp.)
	E. B. Rosa, Burton McCollum, and K. H. Logan
	The Determination of Carbon in Steels and Iron by the Barium Carbonate
53.	Titration Method (12 pp.)
	Determination of Ammonia in Illuminating Gas (23 pp.)
	Combustion Method for the Direct Determination of Rubber (11 pp.). L.G. Wesson
	Industrial Gas Calorimetry (150 pp.)
	Iodine Number of Linseed and Petroleum Oils (17 pp.)
31.	W. H. Smith and J. B. Tuttle
z8.	Observations on Finishing Temperatures and Properties of Rails (63 pp.).
	G. K. Burgess, J. J. Crowe, H. S. Rawdon, and R. G. Waltenberg
30.	Analysis of Printing Inks (20 pp.)
	The Veritas Firing Rings (10 pp.)
	Lead Acetate Test for Hydrogen Sulphide in Gas (46 pp.)
	R. S. McBride and J. D. Edwards
42.	Standardization of No. 200 Cement Sieves (51 pp.). R. J. Wig and J. C. Pearson
43.	Hydration of Portland Cement (71 pp.)
44.	Investigation of the Durability of Cement Drain Tile in Alkali Soils (56 pp.).
	R. J Wig and G. M. Williams (with S. H. McCrory, E. C. Bebb, and
	L. R. Ferguson).
45.	A Study of Some Recent Methods for the Determination of Total Sulphur
	in Rubber (16 pp.)
	A Study of the Atterberg Plasticity Method (18 pp.) Charles S. Kinnison
47.	Value of the High Pressure Steam Test of Portland Cements (34 pp.)
	R. J. Wig and H. A. Davis
48.	An Air-Analyser for Determining the Fineness of Portland Cement (74 pp.).
	J. C. Pearson and W. H. Sligh
49.	Emergent Stem Correction for Thermometers in Creosote Oil Distillation
	Flasks (21 pp.)
	Viscosity of Porcelain Bodies High in Feldspar (5 pp.)
	A. V. Bleininger and C. S. Kinnison
31.	Use of Sodium Salts in the Purification of Clays and in the Casting Process
	(44 pp.)
	An Investigation of Fusible Tin Boiler Plugs (37 pp.)
33.	George K. Burgess and Paul D. Merica
	George R. Burgess and Paul D. Merica

[A complete list of Scientific Papers, Circulars, and miscellaneous publications may be obtained free of charge on application to the Bureau of Standards, Washington, D. C.]

